

DIRECT LIQUEFACTION OF PLASTICS AND COLIQUEFACTION OF COAL-PLASTIC MIXTURES

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Introduction

In previous work⁽¹⁾ we have investigated the direct liquefaction of medium and high density polyethylene(PE), polypropylene(PPE), poly(ethylene terephthalate)(PET), and a mixed plastic waste, and the coliquefaction of these plastics with coals of three different ranks. The results established that a solid acid catalyst(HZSM-5 zeolite) was highly active for the liquefaction of the plastics alone, typically giving oil yields of 80-95% and total conversions of 90-100% at temperatures of 430-450 °C. In the coliquefaction experiments, 50:50 mixtures of plastic and coal were used with a tetralin solvent(tetralin:solid = 3:2). Using ~1% of the HZSM-5 catalyst and a nanoscale iron catalyst, oil yields of 50-70% and total conversions of 80-90% were typical. Our earlier work on the coliquefaction of paper(newsprint) with coal⁽²⁾ also established that high total conversions were obtained; however, the gas yields were high, while the oil yields were moderate.

In the current work, we have conducted further investigations of the liquefaction reactions of PE and the coliquefaction reactions of PE, PPE and Black Thunder subbituminous coal. We have also investigated the coliquefaction reactions of PE, PPE, and newsprint. Several different catalysts have been used in these studies. Initial work has been completed on the direct liquefaction of a commingled waste plastic obtained from the American Plastics Council.

Experimental Procedure

The feedstock materials used in the work reported in this paper included medium density polyethylene (PE), polypropylene (PPE), a commingled waste plastic obtained from the American Plastics Council(APC), and a subbituminous coal (Black Thunder). Proximate and ultimate analyses for the coal and APC waste plastic are shown in Table 1. The experiments used 3 types of catalysts: a commercial HZSM-5 zeolite catalyst⁽²⁾, an ultrafine ferrihydrite treated with citric acid(FHYD/CA), and a ternary Al/Si/ferrihydrite with Al:Si:Fe=1:1:18 (FHYD_{0.90}/Al_{0.05}Si_{0.05}). The ultrafine ferrihydrite catalysts are synthesized in our laboratory. For all runs, 1 wt.% of catalyst was added. Dimethyl disulfide (DMDS) was sometimes added to convert the ultrafine ferrihydrite to pyrrhotite during the reaction. The preparation, structure, and liquefaction activity of the ferrihydrite catalysts has been discussed in detail elsewhere^(3,4).

The liquefaction experiments were conducted in tubing bomb reactors with a volume of 50ml which were shaken at 400 rpm in a fluidized sand bath at the desired temperature. The reaction times were 20-60 min. and the atmosphere in the bomb was either hydrogen or nitrogen (cold pressure 100-800 psi). Usually 5 g of plastic or plastic + coal with 7.5 g of solvent(tetralin and/or waste oil) were charged in the tubing bombs. The reactor was cooled in a second sand bath, and gas products were collected and analyzed by gas chromatography⁽⁵⁾. The other products were removed from the reactor with tetrahydrofuran (THF) and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (oils) and pentane insoluble (PA + AS) fractions. Total THF conversion was determined from the amount of insoluble material that remained (residue). Any added catalyst was subtracted from the residue sample weight.

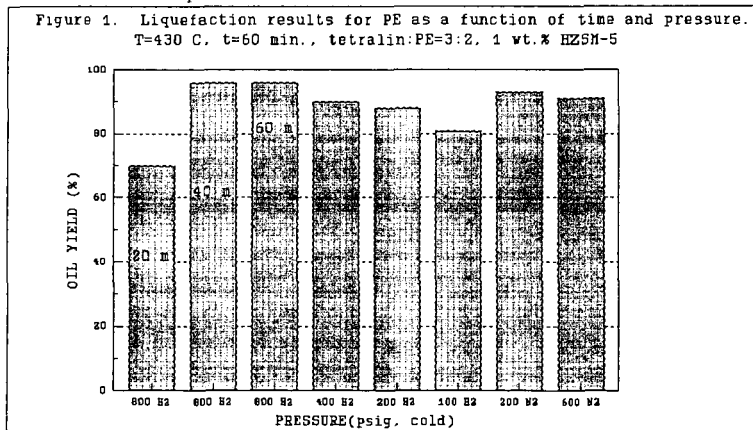
Table 1. Proximate and ultimate analyses of Black Thunder coal and APC commingled waste plastic used in this research.

Proximate ^a	Black Thunder Coal	APC Waste Plastic
% Ash	6.33	0.45
% Volatile	45.40	98.8
% Fixed Carbon	48.27	0.74
Ultimate ^b		
% Carbon	71.59	84.65
% Hydrogen	4.83	13.71
% Nitrogen	1.51	0.65
% Sulfur	0.49	0.01
% Oxygen	15.24	0.98

a = Dry basis, b = Dry ash free basis.

Results and Discussion

Previously, we have shown that a solid acid catalyst(HZSM-5 zeolite) is highly active for the liquefaction of PE, PPE, and mixed waste plastic. Some interesting new results for PE are shown in Figure 1, where it is shown that oil yields are not strongly dependent on hydrogen pressure. Moreover, the oil yield as determined by pentane solubility is as high under nitrogen as it is under hydrogen. The total conversion(THF soluble) was nearly 100% in all cases. Figure 1 also shows the time dependence of the reaction for PE in the presence of HZSM-5.



Our previous paper⁽¹⁾ examined the coliquefaction of a mixed waste plastic with both a bituminous and a subbituminous coal. Oil yields of 60-70% and total conversions of over 90% were observed in the presence of both the HZSM-5 catalyst and an iron catalyst(430 °C, 800 psi H₂-cold, 60 min., tetralin solvent). We are currently studying the response of individual plastic resins to various catalysts and conditions in more detail.

Some typical results are shown in Table 2. PE and PPE both respond strongly to the HZSM-5 catalyst. PPE also responds very well to the citric acid-treated ferrihyrite although PE does not. It is also seen that the mixtures of PE and coal do not liquefy as well as PPE-coal mixtures or as well as we observed previously for a mixed plastic⁽¹⁾. Neither the HZSM-5 or the FHYD/CA catalyst has a strong effect on the liquefaction of PE-coal mixtures.

Table 2. Liquefaction results(yields in wt.%) for medium density polyethylene(PE), polypropylene(PPE), and 50:50 mixtures of PE and PPE with Black Thunder coal.

FEED	CATALYST	T (°C)	OIL	GAS	PA+A	TOT.
PE	NONE	430	26	1	39	65
PE	FHYD/CA	430	33	1	34	68
PE	HZSM-5	430	96	1	2	99
PE/COAL	NONE	430	41	3	26	69
PE/COAL	FHYD/CA	430	42	4	22	68
PE/COAL	HZSM-5	430	41	4	28	72
PPE	NONE	420	83	<1	4	88
PPE	FHYD/CA	425	98	2	0	100
PPE	HZSM-5	425	100	<1	0	100
PPE/COAL	HZSM-5	430	71	4	18	93

Some interesting results for a commingled waste plastic provided by the American Plastics Council are shown in Table 3. Here, we have examined the effect of varying both the catalyst and the solvent. It is seen that at 445 °C the nature of the solvent has a larger effect on the oil yield and total conversion than the catalyst. Both catalysts are moderately effective at this temperature; however, the solvent has a much larger effect, with the oil yields increasing from 30-40% to ~90% as tetralin is replaced with a waste motor oil.

Paper and other lignocellulosic wastes constitute a major fraction of the organic portion of municipal wastes. Previous work has focused on the coliquefaction of coal with lignocellulosic materials by two approaches: Route A used H₂, a molybdenum catalyst and tetralin, while Route B used CO and water in the presence of alkali.⁽²⁾ Both approaches gave good results, although an improvement in product quality was achieved via Route B.

Table 3. Liquefaction results(yields in wt.%) for APC waste plastic with different solvents and catalysts. Experiments conducted at 445 °C, 800 psig H₂(cold) in a tubing bomb, with 7.5 g of solvent and 5 g of plastic.

FEED	CAT.	SOLV.	OIL+ GAS	OIL	GAS	PA+AS	TOTAL
W.PL	HZSM-5	OIL-7.5	89.3			5.1	94.4
W.PL	HZSM-5	TET-2.5 OIL-5.0	88.4			5.7	94.1
W.PL	HZSM-5	TET-5.0 OIL-2.5	66.8	63.7	3.1	17.8	84.6
W.PL	HZSM-5	TET-7.5	42.9			12.3	55.2
W.PL	NONE	OIL-7.5	87.1			7.9	95.0
W.PL	NONE	TET-2.5 OIL-5.0	48.6			27.1	75.7
W.PL	NONE	TET-5.0 OIL-2.5	51.0	48.3	2.7	15.2	66.2
W.PL	NONE	TET-7.5	35.8			23.2	58.9
W.PL	FHYD AlSi	OIL-7.5	90.9			4.8	95.7
W.PL	FHYD AlSi	TET-2.5 OIL-5.0	61.8	58.4	3.4	21.2	83.0
W.PL	PHYD AlSi	TET-5.0 OIL-2.5	51.2	48.6	2.6	22.2	73.4
W.PL	FHYD AlSi	TET-7.5	30.2			16.5	46.7

In more recent work, a high conversion of plastics such as polypropylene, polystyrene and polyethylene terephthalate was achieved at 400 °C using Route B. With Route A, however, the conversion of polypropylene did not exceed 20% at 400 °C. Coliquefaction of coal and polypropylene in Route B showed an increase in the overall oil product and a decrease in the asphaltene fraction from coal. A similar effect was observed in the liquefaction of polypropylene and newsprint using Route B. Oxygen contents of liquid fuels from biomass are usually high, especially using the Route A process. However, the oxygen content of the oil product from Route B was less than 9% because of decarboxylation. The oxygen content of the oil from the coprocessing of polypropylene and newsprint was 3.5%.

Summary

New results for plastics liquefaction and coal-plastic coliquefaction suggest that the nature of the plastic, the solvent, and the reaction atmosphere can all have a significant on product yields. A thorough experimental matrix is needed to explore this parameter space. Further catalyst development aimed at producing cheaper, more robust catalysts for coal-waste plastic coliquefaction is required.

References:

1. M.M. Taghiei, Z. Feng, F.E. Huggins, and G.P. Huffman, *Energy & Fuels*, **1994**, *8*, 1228-1332.
2. H. Jung, J.W. Tierney, and I. Wender, *ACS Div. Fuel Chem. Preprints*, **1993**, *38(3)*, 880-885.
3. United Catalysts Inc., P.O. Box 32370, Louisville, KY 40232.
4. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, *Energy & Fuels*, **1994**, *8*, 38-43.
5. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, *Energy & Fuels*, **1994**, *8*, 1152-1153.
6. H.G. Sanjay, A.R. Tarrer, and Chad Marks, *Energy & Fuels*, **1994**, *8*, 99-104.
7. C.J. Lafferty, C. Elói, R.K. Anderson, and J.D. Robertson, *ACS Div. Fuel Chem. Preprints*, **1994**, *39(1)*, 812.